ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

QUANTITATIVE EXTRACTION OF ANIONIC TEXTILE DYES BY POLY(N,N- DIALLYL MORPHOLINIUM BROMIDE) HYDROGELS

M.Sc. Thesis by

Chemist Fazlı OKUTAY

Department : Polymer Science and Technology

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

POLY(N,N-DİALLİL MORFOLİNYUM BROMİD) HİDROJELİNİN ANYONİK TEKSTİL BOYALARINI KANTİTATİF EKSTRAKSİYONU

YÜKSEK LİSANS TEZİ

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Anabilim Dalı : Polimer Bilimleri ve Teknolojisi
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Danışman:Prof.Dr.Niyazi BIÇAK

ŞUBAT 2006

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February 2006 **Fazlı OKUTAY**

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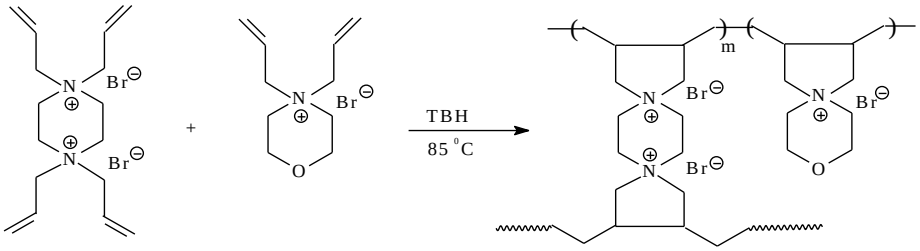

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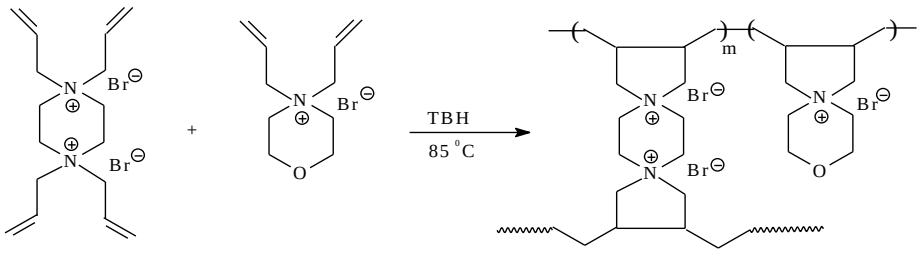
ÖZET

Çevre ve canlı sağlığı açısından tekstil boyama prosesleri sırasında ortaya çıkan atıklarının çevreye zararsız hale getirilip uzaklaştırılması hayati önem arz etmektedir. Bu çalışmada, tekstil boyama prosesi atıkları içerisinde bulanan anyonik esaslı boyaların quaterner amonyum içeren hidrojelle tutulması sağlanmıştır.Sentezlenen polimerik hidrojelin en önemli özelliği aşağıda görüldüğü üzere her bir monomerin 1 ve çapraz bağlayıcının 2 adet kuaterner amonyum gurubu içermesidir.



Bu yöntem Sülfo gurubu içeren boyalar üzerinde oldukça etkin bir tutma kapasitesi göstermiştir. Deneyde Everzol Blue RS/P, Everzol Black GSP, Everzol Red 3BS gibi ticari boyalarla birlikte yapısı bilinen Calgon da kullanılmıştır. İlk olarak hidrojelin maksimum tutma kapasitesi ölçülmüştür. Takip eden çalışmada yüksek konsantrasyonlu çözeltilerde jellerin tutma kapasitesinde değişikliğin olmadığı gözlenmiş bu sonuç dan hareketle boya tutma kapasitesinin Langmuir İzotermine uymaması nedeniyle tutmanın fiziksel değil kimyasal yolla sağlandığı ispat edilmiştir.Çok seyreltik boya çözeltilerindeki boya tutma kapasitesinin çözeltide sıfır boya seviyesini sağladığı deneysel olarak tespit edilmiştir. Hazırlanan aşırı seyreltik çözeltilerde 10 sn içerisinde gözle görülebilir şekilde boyanın sudan arındığı gözlenmiştir. Farklı PH larda ki boya tutma kapasitesi de saptanarak ideal çalışma aralığı tespit edilmiştir.Ticari olarak kullanılan boya tutucularının çoğunun en önemli olumsuz yanlarından biri geri kazanılma özelliklerinin olmamasıdır. Bizde son olarak boya yüklenmiş hidrojel' in geri kazanılıp kazanılamayacağını inceledik . Yaptığımız denemelerde geri kazanılma reaktifi olarak sülfirik asit, anilin ve doymuş sodyum klorür çözeltisi test edilmiştir.. Ancak bunlar arasından en etkin geri kazanılma reaktifi aracının doymuş sodyum klorür çözeltisi (% 86 lar civarında) olduğu saptanmıştır.

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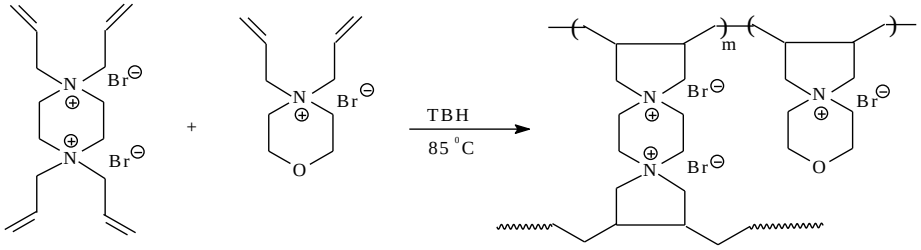

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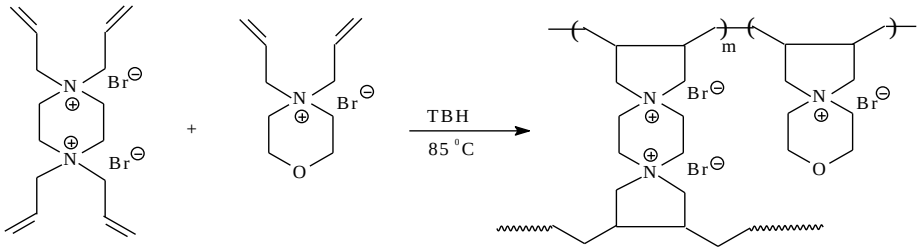

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1. INTRODUCTION

Textile industries consume large volumes of water and chemicals for wet processing of textiles. The chemical reagents used are very diverse in chemical composition, ranging from inorganic compounds to polymers and organic products (Mishra and Tripathy, 1993; Banat et al., 1996; Juang et al., 1996). The presence of very low concentrations of dyes in effluent is highly visible and undesirable (Nigam et al., 2000). There are more than 100,000 commercially available dyes with over 7×10^5 ton of dye-stuff produced annually (Meyer, 1981; Zollinger, 1987). Due to their chemical structure, dyes are resistant to fading on exposure to light, water and many chemicals (Poots and McKay, 1976a; McKay, 1979). Many dyes are difficult to decolourise due to their complex structure and synthetic origin. There are many structural varieties, such as, acidic, basic, disperse, azo, diazo, anthroquinone based and metal complex dyes. Decolouration of textile dye effluent does not occur when treated aerobically by municipal sewerage systems (Willmott et al., 1998).

Through the formation, in 1974 of the Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry (ETAD), aims were established to minimise environmental damage, protect users and consumers and to co-operate fully with government and public concerns over the toxicological impact of their products (Anliker, 1979). Over 90% of some 4000 dyes tested in an ETAD survey had LD_{50} values greater than 2×10^3 mg/kg. The highest rates of toxicity were found amongst basic and diazo direct dyes (Shore, 1996). In Great Britain, such matters are regulated by the Environment Agency (EA) for England and Wales, and the Scottish Environment Protection Agency (SEPTA), (Willmott et al., 1998). Government legislation is becoming more and more stringent, especially in the more developed countries, regarding the removal of dyes from industrial effluents. Environmental policy in UK, Since September 1997, has stated that zero synthetic chemicals should be released into the marine environment. Enforcement of this law will continue to ensure that textile industries treat their dye-containing effluent to the

required standard. European Community (EC) regulations are also becoming more stringent (O'Neill et al.,1999). There are many structural varieties of dyes that fall into either the cationic, nonionic or anionic type. Anionic dyes are the direct, acid and reactive dyes (Mishra and Tripathy, 1993). Brightly coloured, watersoluble reactive and acid dyes are the most problematic, as they tend to pass through conventional treatment systems unaffected (Willmott et al., 1998). Municipal aerobic treatment systems, dependent on biological activity, were found to be inefficient in the removal of these dyes (Moran et al., 1997). Nonionic dyes refer to disperse dyes because they do not ionise in an aqueous medium. Concern arises, as many dyes are made from known carcinogens such as benzidine and other aromatic compounds (Baughman and Perenich, 1988). Weber and Wolfe (1987) demonstrated that azo- and nitro-compounds are reduced in sediments, and similarly (Chung et al. 1978) illustrated their reduction in the intestinal environment, resulting in the formation of toxic amines. Anthroquinone-based dyes are most resistant to degradation due to their fused aromatic ring structure. The ability of some disperse dyes to bioaccumulate has also been demonstrated (Baughman and Perenich, 1988). This review illustrates the critical study of the most widely used methods of dye removal from dye-containing industrial effluents. Currently the main methods of textile dye treatment are by physical and chemical means (Table 1.1) with research concentrating on cheaper effective alternatives.

Table 1.1 Advantages and disadvantages of the current methods of dye removal from industrial effluents

Physical/chemical methods	Advantages	Disadvantages
Fentons reagent	Effective decolourisation of both soluble and insoluble dyes	Sludge generation
Ozonation	Applied in gaseous state: no alteration of volume	Short half-life (20 min)
Photochemical	No sludge production	Formation of by-products
NaOCl	Initiates and accelerates azo-bond cleavage	Release of aromatic amines
Cucurbituril	Good sorption capacity for various dyes	High cost
Electrochemical destruction	Breakdown compounds are non-hazardous	High cost of electricity
Activated carbon	Good removal of wide variety of dyes	Very expensive
Peat	Good adsorbent due to cellular structure	Specific surface areas for adsorption are lower than activated carbon
Wood chips	Good sorption capacity for acid dyes	Requires long retention times

Silica gel	Effective for basic dye removal	Side reactions prevent commercial application
Membrane filtration	Removes all dye types	Concentrated sludge production
Ion exchange	Regeneration: no adsorbent loss	Not effective for all dyes
Irradiation	Effective oxidation at lab scale	Requires a lot of dissolved O_2
Electrokinetic coagulation	Economically feasible	High sludge production

1.1 Aim of this study

The present study is aimed at removal of anionic textile dyes from aqueous wastes by using new cationic hydrogels with high density of quaternary ammonium groups.(i.e 4. $mmol.g^{-1}$). Since the dye sorption capacity of the cationic polymer is proportional to the quaternary group density, we have prepared crosslinked copolymer of N,N-diallyl morpholinium bromide (DAM) with N,N,N',N'-Tetraallyl piperazinium dibromide (TAP) possesing high density of the quaternary ammonium groups. Such a copolymerization yields fully charged polymers constituting with cationic charges in each repeating unit. Polymerization of such monomers are known to proceed by cyclization of the allyl groups yielding pyrazolinium groups in each repeating unit. In the study dye sorption ability crosslinked hydrogel constituting with 10% TAP (mol/mol) has been tested using commercial textile dyes such as Everzol Blue RS/P, Everzol Black GSP and Everzol Red 3BS. It has been observed that capacities of the cationic polyelectrolyte is as high as 1 gr dye per gram of the dry sorbent. Such an unusually high dye sorption is being reported for the first time.More interesting is that , when the dye content of the solution is lower than the capacity, optically clear solutions are obtained. This reveals that, comon sorption isotherms are not applicable in this process.In the study , the dye sorption characteristic of the quaternary ammonium polymer have been studied in various conditions.Moreover regenerability of the dye loaded samples has been studied.Capacities were assayed by colorimetrical analyses of the residual dye contents of the dye solutions. In the analyses, diminushing absorbance maxima of each dye compound were monitored for determination of the dye contents of the

aqueous solutions. It has been observed that, among the spliting agents saturated NaCl solution was found to be most effective.

2.THEORETICAL PART

2.1 Chemical methods

2.1.1 Oxidative processes

This is the most commonly used method of decolourisation by chemical means. This is mainly due to its simplicity of application. The main oxidising agent is usually hydrogen peroxide (H_2O_2). This agent needs to be activated by some means, for example, ultra violet light. Many methods of chemical decolourisation vary depending on the way in which the H_2O_2 is activated (Slokar and Le Marechal, 1997). Chemical oxidation removes the dye from the dye-containing effluent by

oxidation resulting in aromatic ring cleavage of the dye molecules (Raghavacharya, 1997).

2.1.1.1 H_2O_2-Fe(II) salts (Fentons reagent)

Fentons reagent is a suitable chemical means of treating wastewaters which are resistant to biological treatment or are poisonous to live biomass (Slokar and LeMarechal, 1997). Chemical separation uses the action of sorption or bonding to remove dissolved dyes from wastewater and has been shown to be effective in decolourising both soluble and insoluble dyes (Pak and Chang, 1999). One major disadvantage of this method is sludge generation through the flocculation of the reagent and the dye molecules. The sludge, which contains the concentrated impurities, still requires disposal. It has conventionally been incinerated to produce power, but such disposal is seen by some to be far from environmentally friendly. The performance is dependent on the final floc formation and its settling quality, although cationic dyes do not coagulate at all. Acid, direct, vat, mordant and reactive dyes usually coagulate, but the resulting floc is of poor quality and does not settle well, yielding mediocre results (Raghavacharya, 1997).

2.1.1.2 Ozonation

The use of ozone was first pioneered in the early 1970s, and it is a very good oxidising agent due to its high instability (oxidation potential, 2.07) compared to chlorine, another oxidising agent (1.36), and H_2O_2 (1.78). Oxidation by ozone is capable of degrading chlorinated hydrocarbons, phenols, pesticides and aromatic hydrocarbons (Lin and Lin, 1993; Xu and Lebrun,1999). The dosage applied to the dye-containing effluent is dependent on the total colour and residual COD to be removed with no residue or sludge formation (Ince and Gonenc, 1997) and no toxic metabolites (Gahr et al.,1994). Ozonation leaves the effluent with no colour and low COD suitable for discharge into environmental waterways (Xu and Lebrun, 1999). This method shows a preference for double-bonded dye molecules (Slokar and Le

Marechal, 1997). One major advantage is that ozone can be applied in its gaseous state and therefore does not increase the volume of wastewater and sludge. Chromophore groups in the dyes are generally organic compounds with conjugated double bonds that can be broken down forming smaller molecules, resulting in reduced colouration (Peralto-Zamora et al., 1999). These smaller molecules may have increased carcinogenic or toxic properties, and so ozonation may be used alongside a physical method to prevent this. Decolouration occurs in a relatively short time. A disadvantage of ozonation is its short half-life, typically being 20 min. This time can be further shortened if dyes are present, with stability being affected by the presence of salts, pH, and temperature. In alkaline conditions, ozone decomposition is accelerated, and so careful monitoring of the effluent pH is required (Slokar and Le Marechal, 1997). Better results can be achieved using irradiation (Gro. and Byung, 1989) or with a membrane filtration technique (Lopez et al., 1999). One of the major drawbacks with ozonation is cost, continuous ozonation is required due to its short half-line (Xu and Lebrun, 1999).

2.1.1.3 Photochemical

This method degrades dye molecules to CO_2 and H_2O (Yang et al., 1998; Peralto-Zamora et al., 1999) by UV treatment in the presence of H_2O_2. Degradation is caused by the production of high concentrations of hydroxyl radicals. UV light may be used to activate chemicals, such as H_2O_2, and the rate of dye removal is influenced by the intensity of the UV radiation, pH, dye structure and the dye bath composition (Slokar and Le Marechal, 1997). This may be set-up in a batch or continuous column unit (Namboodri and Walsh, 1996). Depending on initial materials and the extent of the decolourisation treatment, additional by-products, such as, halides, metals, inorganic acids, organic aldehydes and organic acids, may be produced (Yang et al., 1998). There are advantages of photochemical treatment of dye-containing efluent; no sludge is produced and foul odours are greatly reduced. UV light activates the destruction of H_2O_2 into two hydroxy radicals. This causes the chemical oxidation of organic material.

2.1.1.4 Sodium hypochloride (NaOCl)

This method attacks at the amino group of the dye molecule by the Cl^-. It initiates and accelerates azobond cleavage. This method is unsuitable for disperse dyes. An increase in decolouration is seen with an increase in Cl concentration. The use of Cl for dye removal is becoming less frequent due to the negative effects it has when released into waterways (Slokar and Le Marechal, 1997) and the release of aromatic amines which are carcinogenic or otherwise toxic molecules (Banat et al., 1999).

2.1.1.5 Cucurbituril

Cucurbituril was first mentioned by Behrand et al. (1905), and then rediscovered in the 1980s by Freeman et al. (1981). It is a cyclic polymer of glycoluril and formaldehyde (Karcher et al., 1999a,b). Cucurbituril, so named, because its structure is shaped like a pumpkin (a member of the plant family Cucurbitaceae). The uril, indicates that a urea monomer is also part of this compound. Buschmann (1992) showed extraordinarily good sorption capacity of cucurbituril for various types of textile dyes. Cucurbituril is known to form host-guest complexes with aromatic compounds (Mock, 1995) and this may be the mechanism for reactive dye adsorption. Another proposed mechanism is based on hydrophobic interactions or the formation of insoluble cucurbiturildye-cation aggregates since adsorption occurs reasonably fast. To be industrially feasible, cucurbituril would need to be incorporated into fixed bed sorption filters (Karcher et al., 1999b). Like many other chemical methods, cost is a major disadvantage.

2.1.1.6 Electrochemical destruction

This is a relatively new technique, which was developed in the mid 1990s. It has somesignificant advantages for use as an effective method for dye removal. There is little or no consumption of chemicals and no sludge build up. The breakdown metabolites are generally not hazardous leaving it safe for treated wastewaters to be released back into water ways. It shows efficient and economical removal of dyes and a high efficiency for colour removal and degradation of recalcitrant pollutants (Ogutveren and Kaparal, 1994; Pelegrini et al.,1999). Relatively high flow rates cause a direct decrease in dye removal, and the cost of electricity used is comparable to the price of chemicals.

2.2 Physical treatments

2.2.1 Adsorption

Adsorption techniques have gained favour recently due to their efficiency in the removal of pollutants too stable for conventional methods. Adsorption produces a high quality product, and is a process which is economically feasible (Choy et al., 1999). Decolourisation is a result of two mechanisms: adsorption and ion exchange (Slokar and Le Marechal, 1997), and is influenced by many physio-chemical factors, such as, dye/sorbent interaction, sorbent surface area, particle size, temperature, pH, and contact time (Kumar et al., 1998).

2.2.1.1 Activated carbon

This is the most commonly used method of dye removal by adsorption (Nasser and El-Geundi, 1991) and is very e.ective for adsorbing cationic, mordant, and acid dyes and to a slightly lesser extent, dispersed, direct, vat, pigment and reactive dyes (Raghavacharya, 1997; Rao et al., 1994). Performance is dependent on the type of carbon used and the characteristics of the wastewater. Removal rates can be improved by using massive doses, although regeneration or re-use results in a steep reduction in performance, and efficiency of dye removal becomes unpredictable and dependent on massive doses of carbon. Activated carbon, like many other dye-removal treatments, is well suited for one particular waste system and ineffective in another. Activated carbon is expensive. The carbon also has to be reactivated otherwise disposal of the concentrates has to be considered. Reactivation results in 10-15% loss of the sorbent.

2.2.1.2 Peat

The cellular structure of peat makes it an ideal choice as an adsorbent. It has the ability to adsorb transition metals and polar organic compounds from dye-containing efluents. Peat may be seen as a viable adsorbent in countries such as Ireland and UK, where it is widely available. Peat requires no activation, unlike activated carbon, and also costs much less (Poots and McKay, 1976a). Due to activated carbon's powdered nature, it has a much larger surface area, and hence has a better

capacity for adsorption. Spent peat may be burned and utilised for steam raising, or, potentially, as substrate in SSF, for protein enrichment.

2.2.1.3 Wood chips

They show a good adsorption capacity for acid dyes although due to their hardness, it is not as good as other available sorbents (Nigam et al., 2000) and longer contact times are required (Poots and McKay, 1976b). Adsorbed wood is conventionally burnt to generate power although there is potential for SSF of the dyeadsorbed wood chips.

2.2.1.4 Fly ash and coal (mixture)

A high fly ash concentration increases the adsorption rates of the mixture due to increasing the surface area available for adsorption. This combination may be substituted for activated carbon, with a ratio of fly ash:coal, 1:1 (Gupta et al., 1990).

2.2.1.5 Silica gel

An effective material for removing basic dyes, although side reactions, such as air binding and air fouling with particulate matter, prevents it being used commercially.

2.2.1.6 Other materials

The use of these substrates such as natural clay, corn cobs, rice hulls etc., for dye removal is advantageous mainly due to their widespread availability and cheapness. They are economically attractive for dye removal, compared to activated charcoal, with many comparing well in certain situations (Nawar and Doma, 1989; Nasser and El-Geundi, 1991; Nigam et al., 2000). These materials are so cheap regeneration is not necessary and the potential exists for dye-adsorbed materials to be used as substrates in solid state fermentation (SSF) for protein enrichment.

2.2.1.7 Membrane filtration

This method has the ability to clarify, concentrate and, most importantly, to separate dye Continuously from effluent (Mishra and Tripathy, 1993; Xu and Lebrun, 1999). It has some special features unrivalled by other methods; resistance to temperature, an adverse chemical environment, and microbial attack. The concentrated residue

left after separation poses disposal problems, and high capital cost and the possibility of clogging, and membrane replacement are its disadvantages. This method of filtration is suitable for water recycling within a textile dye plant if the effluent contains low concentration of dyes, but it is unable to reduce the dissolved solid content, which makes water re-use a difficult task.

2.2.1.8 Ion exchange

Ion exchange has not been widely used for the treatment of dye-containing effluents, mainly due to the opinion that ion exchangers cannot accommodate a wide range of dyes (Slokar and Le Marechal, 1997). Wastewater is passed over the ion exchange resin until the available exchange sites are saturated. Both cation and anion dyes can be removed from dye-containing effluent this way. Advantages of this method include no loss of adsorbent on regeneration, reclamation of solvent after use and the removal of soluble dyes. A major disadvantage is cost. Organic solvents are expensive, and the ion exchange method is not very effective for disperse dyes (Mishra and Tripathy, 1993).

2.2.1.9 Irradiation

Sufficient quantities of dissolved oxygen are required for organic substances to be broken down effectively by radiation. The dissolved oxygen is consumed very rapidly and so a constant and adequate supply is required. This has an effect on cost. Dye-containing effluent may be treated in a dual-tube bubbling rector. This method showed that some dyes and phenolic molecules can be oxidised effectively at a laboratory scale only (Hosono et al., 1993).

2.2.1.10 Electrokinetic coagulation

This is an economically feasible method of dye removal. It involves the addition of ferrous sulphate and ferric chloride, allowing excellent removal of direct dyes from wastewaters. Unfortunately, poor results with acid dyes, with the high cost of the ferrous sulphate and ferric chloride, means that it is not a widely used method. The optimum coagulant concentration is dependent on the static charge of the dye in solution and difficulty in removing the sludge formed as part of the coagulation is a

problem (Mishra and Tripathy, 1993). Production of large amounts of sludge occurs, and this results in high disposal costs (Gahr et al., 1994)

2.2.1.11 Quaternary Ammonium Polymers

Some natural or synthetic polymers bearing quaternary ammonium groups have been demonstrated to be efficient in removal of anionic textile dyes from water (Lazio 1996) (Hwang M. C.1993)(Antal M.1984.) The dye sorption by those materials is based on Coulombic interaction of the cationic charges on the sorbent with anionic groups of the dye molecules. Dye sorption capacities of these sorbents might be as high as 250 mg per gram of the sorbent.Quaternized chitosan and cellulose derivation such as sunflower stalks Shi, X . et al(1999)Glycidyl trimethyl ammonium chloride has been used to import the quaternary ammonium functions. Increasing quaternary ammonium content has been demonstrated to increase the dye sorption capacities. Interestingly sunflower stalks quaterned with glycidyl trimethyl ammonium chloride has shown to sorp also cationic dye molecules to some extent.Apparently in this case the Coulombic interaction can not be considered as the bases of the dye uptake.Instead Vander Waals interaction of the hydrophopic parts of the sorbent and dye molecules must be responsible for their dye uptake

2.3 Biological treatments

2.3.1 Decolourisation by white-rot fungi

White-rot fungi are those organisms that are able to degrade lignin, the structural polymer found in woody plants (Barr and Aust, 1994). The most widely studied white-rot fungus, in regards to xenobiotic degradation, is Phanerochaete chrysosporium. This fungus is capable of degrading dioxins, polychlorinated biphenyls (PCBs) and other chloro-organics (Chao and Lee,1994; Reddy,1995). Davis et al. (1993) also showed the potential of using P. sordida to treat creosote contaminated soil. Kirby (1999) has shown that P. chrysosporium had the ability to decolourise artificial textile effluent by up to 99% within 7 days. White-rot fungi are able to degrade dyes using enzymes, such as lignin peroxidases (LiP), manganese dependent peroxidases (MnP). Other enzymes used for this purpose include H_2O_2-

producing enzymes, such as, glucose-1-oxidase and glucose-2-oxidase, along with laccase, and a phenoloxidase enzyme (Archibald and Roy, 1992; Thurston, 1994; Schliephake and Lonergan, 1996; Kirby, 1999). These are the same enzymes used for the lignin degradation (Lonergan, 1992; Barr and Aust, 1994; Reddy, 1995). Azo dyes, the largest class of commercially produced dyes, are not readily degraded by micro-organisms but these can be degraded by P. chrysosporium (Paszczynski and Crawford, 1995). Other fungi such as, Hirschioporus larincinus, Inonotus hispidus, Phlebia tremellosa and Coriolus versicolor have also been shown to decolourise dye-containing effluent (Banat et al., 1996; Kirby, 1999). Although white-rot fungi have been shown to decolourise dyes in liquid fermentations, enzyme production has also been shown to be unreliable. This is mainly due to the unfamiliar environment of liquid fermentations. The ability to utilise these fungi in their natural environment means that they are more likely to be more effective in SSF.

2.3.2 Other microbial cultures

Mixed bacterial cultures from a wide variety of habitats have also been shown to decolourise the diazolinked chromophore of dye molecules in 15 days (Knapp and Newby, 1995). Nigam and Marchant (1995) and Nigam et al. (1996) demonstrated that a mixture of dyes were decolourised by anaerobic bacteria in 24-30 h, using free growing cells or in the form of biofilms on various support materials. Ogawa and Yatome (1990) also demonstrated the use of bacteria for azo dye biodegradation. These microbial systems have the drawback of requiring a fermentation process, and are therefore unable to cope with larger volumes of textile effluents. The ability of bacteria to metabolise azo dyes has been investigated by a number of research groups. Under aerobic conditions azo dyes are not readily metabolised although Kulla (1981), reported the ability of Pseudomonas strains to aerobically degrade certain azo dyes. However, the intermediates formed by these degradative steps resulted in disruption of metabolic pathways and the dyes were not actually mineralised. Under anaerobic conditions, such as anoxic sediments, many bacteria gratuitously reduce azo dyes reportedly by the activity of unspecific, soluble, cytoplasmic reductases, known as azo reductases. These enzymes are reported to result in the production of colourless aromatic amines which may be toxic, mutagenic, and possibly carcinogenic to animals. Increasingly literature evidence

suggests that additional processes may also be involved in azo dye reduction. It has been reported that many bacteria reduce a variety of sulfonated and non-sulfonated azo dyes under anaerobic conditions without specificity of any significance. In addition many highly charged and high molecular-sized sulfonated and polymeric azo dyes are unlikely to pass the cell membrane. Taken together both pieces of evidence point to the existence of a reducing activity which is not dependent on the intracellular availability of the azo dye (Keck et al., 1997). This hypothesis was supported by work at the University of Stuttgart, Germany, which isolated a strain of Sphingomonas capable of using redox mediators generated during the aerobic metabolism of 2-naphthalenesulfonate to facilitate a 20-fold increase in its ability to reduce the sulfonated azo dye amaranth (Keck et al., 1997). These redox mediators were found to be decomposition products of 1,2-dihydroxynaphthalene and were able to anaerobically shuttle reduction equivalents from the bacterial cells to the extracellular azo dye. Subsequently this group found that their isolate Sphingomonas sp strain BN6 possessed both cytoplasmic and membrane-bound azo-reductase activities (Kudlich et al., 1997). Yeasts, such as Klyveromyces marxianus, are capable of decolourising dyes. Banat et al. (1999) showed that K. marxianus was capable of decolourising Remazol Black B by 78-98%. Zissi et al. (1997) showed that Bacillus subtilis could be used to break down p-aminoazobenzene, a specific azo dye. Further research using mesophilic and thermophilic microbes has also shown them to degrade and decolourise dyes (Nigam et al.,1996; Banat et al., 1997).

2.3.3 Adsorption by living/dead microbial biomass

The uptake or accumulation of chemicals by microbial mass has been termed biosorption (Hu,1992, 1996; Tsezos and Bell, 1989; Kumar et al., 1998). Dead bacteria, yeast and fungi have all been used for the purpose of decolourising dye-containing effluents. Textile dyes vary greatly in their chemistries, and therefore their interactions with micro-organisms depend on the chemistry of a particular dye and the specfic chemistry of the microbial biomass (Polman and Brekenridge, 1996). Depending on the dye and the species of micro-organism used di.erent binding rates and capacities will be observed. It can be said that certain dyes have a particular affinity for binding with microbial species. It had been observed that

biomass derived from the thermotolerant ethanol-producing yeast strain, K. marxianus IMB3, exhibited a relatively high affinity for heavy metals (Riordan et al., 1997; Bustard and McHale, 1998; Riordan and McHale, 1998). Biosorption capacities showed that this type of biomass had a signficantly high affinity for dye removal, and so widened the spectrum of use for biomass (Bustard et al., 1998). The use of biomass has its advantages, especially if the dye-containing effluent is very toxic. Biomass adsorption is effective when conditions are not always favourable for the growth and maintenance of the microbial population (Modak and Natarajan, 1995). Adsorption by biomass occurs by ion exchange. Hu (1992) demonstrated the ability of bacterial cells to adsorb reactive dyes. Zhou and Zimmerman (1993) used actinomyces as an adsorbent for decolourisation of effluents containing anthroquinone, phalocyanine and azo dyes. Biosorption tends to occur reasonably quickly: a few minutes in algae to a few hours in bacteria (Hu,1996). This is likely to be due to an increase in surface area caused by cell rupture during autoclaving (Polman and Brekenridge, 1996).

2.3.4 Anaerobic textile-dye bioremediation systems

Azo dyes make up 60-70% of all textile dyestuffs (Carliell et al., 1995). Azo dyes are soluble in solution, and are not removed via conventional biological treatments. Reactive dyes have been identified as the most problematic compounds in textile dye effluents (Carliell et al., 1996, 1994). Anaerobic bioremediation allows azo and other water-soluble dyes to be decolourised. This decolourisation involves an oxidation-reduction reaction with hydrogen rather than free molecular oxygen in aerobic systems. Typically, anaerobic breakdown yields methane and hydrogen sulphide (Carliell et al., 1996). Azo dye acts as an oxidising agent for the reduced flavin nucleotides of the microbial electron chain and is reduced and decolourised concurrently with reoxidation of the reduced flavin nucleotides. In order for this to occur, additional carbon is required in order for decolourisation to proceed at a viable rate. This additional carbon is converted to methane and carbon dioxide,

releasing electrons. These electrons cascade down the electron transport chain to a final electron acceptor, in this case, the azo-reactive dye. The electrons react with the dye reducing the azo bonds, and ultimately causing decolourisation (Carliell et al., 1996). In lab-scale studies glucose has been added to provide a source of carbon. This additional carbon supplementation may be a limiting factor when this technology is scaled-up. Anaerobic degradation of textile dyes yields only azo reduction. Mineralisation does not occur. It has been shown that azo- and nitro-components are reduced in the sediments and in the intestinal environment, resulting in the regeneration of the parent toxic amines (Banat et al., 1996). Therefore, careful monitoring is required before treated wastewater is released into waterways.

3.EXPERİMENTAL PART

3.1. Materials and Instruments

All the chemicals used were analytical grade chemical products: morpholine (Fluka), piperazine (Fluka), allyl chloride (E.Merck), allyl bromide (Fluka), $K_2S_2O_8$ (E. Merck), Dimethyl sulfoxide (DMSO) (E. Merck), tert-butyl hydroperoxide (Aldrich)

otherchemicals and solvents were used without further purification. Distilled water (conductivity 2 μS) was used for the polymerizations. ^{1}H-NMR spectra were recorded on Bruker Model spectrometer in D_2O solvent; FT-IR spectra were taken by using Mattson 1000 spectrometer, with KBr disc. Schumadzu UV / VIS 160 A S spectrofotometer

3.2 Preparation of N-allyl morpholine (AML)

This compound was prepared from morpholine and allyl chloride as described elsewhere (Bicak N et al.,1998). The liquid product boils at 147-151 ^{0}C.

3.3 Synthesis of N,N-diallyl morpholinium bromide (DAM)

This was prepared by quaternization of AML with allyl bromide as described in our previous article (Bicak N et al.,1999) . A typical procedure is as follows: 35 ml (0.41 mol) of allyl bromide was placed in a flask in an ice bath. While stirring 66 ml (0.4 mol) of AML was added dropwise to the flask over about 30 min. White precipitates were observed after 1 h of stirring. Stirring was continued for another 3 h. Then the flask was closed tightly and left to stand for 5 days at room temperature. The white crystalline mass formed was dispersed in 50 ml of diethyl ether and filtered. It was washed with ether and dried under vacuum at room temperature for 24 h, yield 99.2 g (96%), mp: 210 ^{0}C . The product is very hy-groscopic and it is soluble in water, DMF, DMSO, methanol, ethanol and butanol and insoluble in ether, cyclohexane, benzene and toluene. Elemental microanalysis, found (calculated for $C_{10}H_{18}NOBr$), C: 47.75% (48.38%), H: 7.95% (7.26%), N: 5.44% (5.64%). ^{1}H-NMR, ^{13}C-NMR and FT-IR spectra of the monomer are given in [Figs. A.1 ,A.2, A.3(a)], respectively.

3.4. Preparation of N,N'-Diallyl Piperazin (DAP)

Piperazine (43 g, 0.5 mol) was dissolved in 150 mL of methanol in a 1 L volume of canonical flask. The flask was placed in an ice bath. While stirring vigorously, 83 mL (1.02 mol) allyl chloride was added dropwise in about 40 min through a dropping funnel. After 1 h of stirring a white precipitate was observed. Stirring was continued for 13 h. The solution of 56 g (1.0 mol) KOH in 200 mL methanol was added

portionwise to the mixture. The first portion 100 mL was added after 1 h and the remaining was divided in two equal portions and was added 3 and 5 h later. Stirring was continued overnight at room temperature. KCl was filtered and methanol was distilled off by a rotavapor. The liquor was transferred into 250 mL volume of distillation flask and distilled under diminished pressure. The fraction boiling at 108–111 °C/(1 mm) was collected. Yield: 57 g (68 %). Elementary microanalysis: Calcd. for $C_{10}H_{18}N_2$. Found: C, 72.3% (72.1); H,10.8% (10.4); N, 16.9% (16.0). ^{1}H NMR and FTIR spectra of the product are given in[Figures A.4 and A.5(a)] , respectively.

3.5 Preparation of N,N,N',N'-Tetra Allyl Piperazinium Dibromide (TAP)

Under an efficient fume cupboard, 40 g (0.24 mol) *N,N*-diallyl piperazine was put into 250 mL volume flask in an ice bath. While stirring vigorously by a magnetic stirring bar, 63 mL (0.26 mol) allyl bromide was added to the flask dropwise in about 40 min. The mixture was stirred for 4 h. At that time, an oily phase was separated. Then the reaction content was left to stand for 5 days at room temperature. The hard crystalline product formed was filtered as quickly as possible and washed with ether. It was dried at 40 °C under vacuum for 24 h. Yield: 96.2 g (98%). mp: 205 °C . The quaternization product is very hygroscopic and very soluble in H_2O and DMF, insoluble in benzene and toluene, and slightly soluble in methanol. Elementary microanalysis:Calcd. for $C_{16}H_{28}$- N_2Br_2. Found: C, 47.0% (47.4); H, 6.86% (7.03); N, 6.86% (7.16). ^{1}H NMR and FTIR spectra of the product are given in [Figures A.6 and A.5(b)], respectively.

3.6 Copolymerization with N,N-Diallyl Morpholinium Bromide

Crosslinking copolymerization of N,N-Diallyl Morpholinium Bromide with N,N,N',N'-Tetra Allyl Piperazinium Dibromide (TAP) was carried out according to the procedure is as described (Bicak N et al.,1999)**.** The copolymerization was carried out in concentrated (60%) aqueous solutions at 85 °C using TBH as radical initiator. Using different monomer–comonomer combinations,the copolymerization was conducted until gelation occurred. A typical is as follows: 2.23 g (9.0mmol) DAM and 0.4 g (1.0 mmol) TAP are placed in a 50 mL volume of two-necked flask attached to a reflux condenser. The flask is mounted in an oil bath of which the temperature is

adjusted by a contact thermometer. Then 1.8 mL water is added to the flask and heated at 50 °C until a clear solution is observed. While stirring, the solution is purged with nitrogen and 0.05 mL TBH is added by means of a micropipette. The temperature is raised up to 85 °C and the stirring is continued at this temperature until gelation occurs (34 min). The clear hydrogel formed is broken up by a glass rod and transferred into a sintered glass funnel. The gel is washed with excess of water and dried at 60 °C for 24 h under vacuum. Yield: 2.1 g (80.0%). The gel obtained is sticky and this causes inevitable mechanical losses in handling.

3.7 Swelling Experiments

After synthesis, the dry hydrogels were placed in syntherid glass funnels, which were immersed in distilled water. The swellings of the hydrogels were monitored by mass measurements every 10 min; approximately 1 h was enough to reach equilibrium swelling. Once equilibrium was attained, the hydrogels were weighed, dried at 60 °C in vacuum for 24 h, and re-weighed. The swelling ratio is defined as the mass ratio of swollen hydrogel to dry hydrogel.

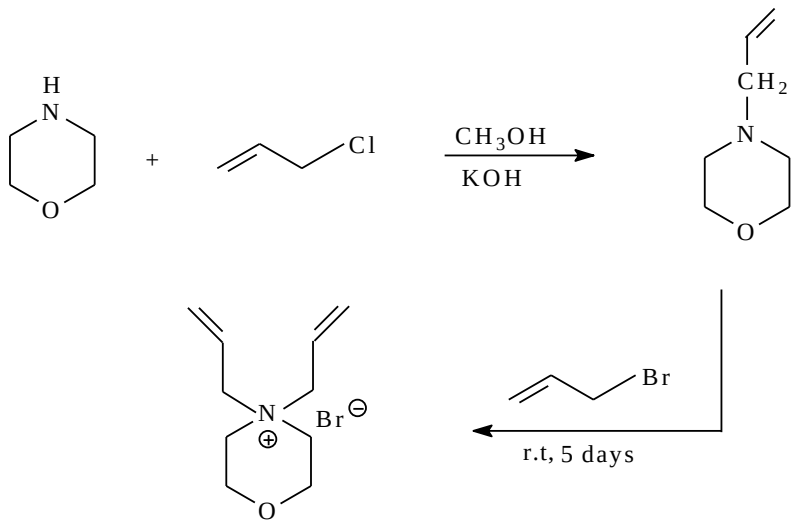
3.8 Dye uptake measurements of the hydrogels

Dye capacities of the hydrogels were determined by mixing weighed amount of polymer sample (0.2 g) with 20 mL aqueous dye solution (0.01 M). In these experiments everzol red , everzol black , everzol blue , calgon were used as dye. The mixture was stirred for 24 h and the filtered. The dye concentrations were determined colorimetrically in different wavelength. The dye loading capacities were calculated from the initial and final dye contents of the solution. 1 ml volume of the filtrate was used for determination of the residual dye.

4. RESULTS AND DISCUSSION

4.1 Preaparation of DAM (diallyl morpholinium bromide)

The monomer DAM can be prepared by quaternization of N-allyl morpholine with allyl bromide.



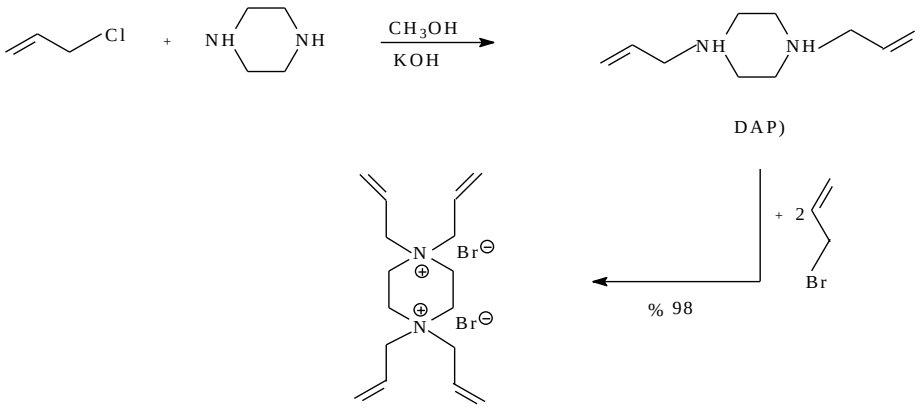
Scheme 4.1 Preaparation of DAM (diallyl morpholinium bromide)

However, when the reagents interact at room temperature as in the original procedure described by Butler, severe explosions occur within 30 min contact time. For safety considerations, we have observed that efficient cooling is essential at the beginning of the reaction. Then the reaction proceeds smoothly at room temperature and five days of standing gives almost quantitative yields (Scheme 4.1). With solvents such as methanol and ethanol, however, the yields are always low even at prolonged times. Elemental microanalysis and NMR spectra of the monomer clearly establish its structure. Thus, in the ^{1}H-NMR spectrum [Fig. A.1] the multiplet at 6.1 ppm represents –CH= protons of the allyl group. The second multiplet centered at

5.7 ppm shows $=CH_2$ proton signals. Protons of the allylic carbon give a doublet at 4.1 ppm. Two triplets at 4 and 3.42 ppm indicate $–N-CH_2-$ and $–OCH_2-$ protons of the morpholine ring, respectively. ^{13}C-NMR spectrum of this compound in [Fig A. 2] represents five types of carbon atoms as expected. The carbons of morpholine rings are observed at 57 ppm (-C-N-) and at 60 ppm (-C-O-) the allylic carbons give a signal at 60.5 ppm. $CH_2=$ and CH= carbon signals appear at 125 and 128 ppm, respectively. In the FT-IR spectrum of the monomer [Fig. A.3.(a)], the intense peaks at 3070 and 1680 cm^{-1} indicate =C- H and C=C stretching vibrations of the allyl groups. Out of plane bending vibrations of olefinic C-H groups are observed as sharp peaks at 830 and 950 cm^{-1}, which indicates unsaturation.

4.2 Preparation of the Ionic Crosslinker

The reaction of piperazine with two equivalents of allyl chloride gives rise to *N,N*-diallyl piperazine (DAP) as shown in Scheme 4.2. The reaction proceeds smoothly in methanol solution.



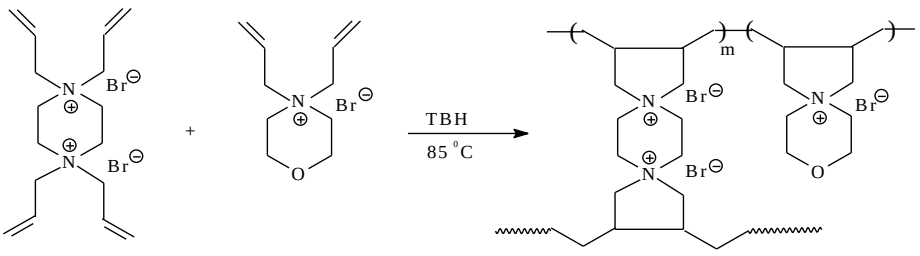
Scheme 4.2 Preparation of the Ionic Crosslinker

Equivalent amounts of KOH is added portion wise to avoid any probable isomerization of the allyl groups. The yield of pure liquid product, after distillation, is 68%. Quaternization of DAP with allyl chloride gives *N,N,N',N'*-tetraallyl piperazinium chloride as a very hygroscopic solid. Best yields are obtained by direct interaction of the reagents at 0 °C. However, when the reaction is performed at room temperature, violent explosions occur in about 10 min of contacting times. To avoid

explosions, in this study, we have also tried to use solvents as described in the original procedure (Butler, G.B., Bunch, R.L.1949). However, these experiments with or without heating always gave low yields (20–40%) in our hands. ^{1}H NMR spectra of DAP and TAP in (Fig. A.4) , [Fig A.6] confirm the structures proposed. ^{1}H NMR spectra of DAP in [Fig. A.1] show four different proton signals as expected. Piperazine ring protons of the DAP are observed at 2.6 ppm as a sharp singlet. The protons of the allylic carbon give a doublet at 3.1 ppm. The multiples at 5.3 and 5.9 ppm indicate protons of CH_2= and =CH- groups, respectively. In the NMR spectra of TAP [Fig. A.6] all the proton signals shift to lower fields because of quaternization. In this case, the singlet of the piperazine ring protons shifts to 4.1 ppm and the doublet of the protons of allylic groups appears at 4.4 ppm. Slight down shifts are observed for the olephinic-proton signals after quaternization and these are observed at 6.0 and 6.2 ppm, respectively. These transformations can also be followed by their FTIR spectra shown in [Figure A.5 (a,b)]. In both spectra, characteristic C=C and C-H stretching vibrations are observed at about 1680 and 3080 cm $^{-1}$, respectively. In the FTIR spectra of DAP [Fig. A.5(a)] C-N stretching vibrations represent intense band at 1100 cm $^{-1}$ .Whereas, for the case of TAP, this band [Fig. A.5(b)] is observed at 1150 cm^{-1} because of quaternization.

4.3 Copolymerization with N,N-Diallyl Morpholinium Bromide (DAM)

Homopolymerization of TAP and its copolymerization with DAM in concentrated aqueous solutions (60%) with *t*-butyl hydroperoxide initiator at 85 °C give transparent hydrogels in high yields. No precipitation and any heterogeneity is observed in the polymerizations. The rigid gels obtained are completely homogeneous and transparent.The structures of the crosslinked polymer gels can be depicted as shown in Scheme 4.3.



Scheme 4.3 Copolymerization with N,N-Diallyl Morpholinium Bromide (DAM)

Low yields are obtained, however, in more dlute solutions because of strong Coulombic repulsion between the monomers as has been demonstrated for the polymerization of some quaternary diallyl ammonium monomers. Indeed, with 10% of total monomer concentrations, no gels were obtained even after 8 h of reaction times. When the total monomer concentration was raised to 20%, the dry gel yields were about 10–20%. In the reaction condition studied, as the ratio of the crosslinker, TAP to the DAM, is increased, the gelation time reduces significantly (Table 4.1). In the FTIR spectra of these gels [Fig. A.5(d)] the olephinic C-H stretching vibrations of the monomers, at 3080 cm^{-1} do not disappear completely, which imply some residual unsaturations. Intensities of these bands are in accordance with the crosslinker ratios. In the case for 5% of the crosslinker ratio only a weak band is observed for the homopolymer of the crosslinker, TAP. The surface area of this band is about 8.3% of its monomer. Obviously, these residual unsaturations can be ascribed to the unreacted allyl groups of the crosslinker. Interestingly, after a successive washing of the homopolymer of TAP, intensity of this band becomes somewhat weaker than its original. This reveals that some of the unreacted monomer remain entrapped in the gel matrix and washing presumably causes its extraction to some extent.

4.3.1 Determination of the Residual Unsaturation in the Copolymers

The residual unsaturations were estimated roughly by comparison of C-H stretching vibrations of the polymers and monomers, observed at 3080 cm^{-1}, as described in the literature (Spurr et al., 1959) The bromine addition method was also considered to determine unreacted allyl groups in the polymer. But this method seemed not to be satisfactory due to slow diffusion of the bromine into the crosslinked polymer matrix and its probable substitution on the morpholine ring. In the procedure, 4.08 mg (1025 mol) TAP and 4.8 mg (1024 mol) DAM were mixed in a mortar quickly and 1 mg, 2 mg, 3 mg, and 5 mg samples were weighed and each mixed separately with 300 mg of dry KBr samples. These were mixed homogeneously by grinding and their pellets were prepared as usual. A calibration curve of unsaturation was prepared based on the intensities of the IR bands at 3080 cm^{-1}. Using band

intensities of the copolymers at some frequency, the residual unsaturations per gram were found by the calibration curve. The results found were tabulated in Table 4.1.

Table 4.1 Residual Unsaturation in the Copolymers

Run	**DAM/TAP (mol/mol)**	**TBH/T[a] (mol/mol)**	**Gelation time (min)[b]**	**Swelling in H_20 (W/W_0)**	**Ionic[c] content mmol/g**	**Residual unsaturation**
1	9.5/0.5	$1,2x10^{-2}$	65	16,2	4,10	<1,2%
2	9/1	$1,2x10^{-2}$	34	14,1	4,16	<1,5%
3	8/2	$1,2x10^{-2}$	18	10,7	4,28	7,1%
4	7/3	$1,2x10^{-2}$	14	8,8	4,90	8,3%

Table Charecteristics of Strong Cationic Hydrogels
[a] T: total monomer (mol)
[b]With %60 (w/w_0) total monomer concentration
[c]Quaternary amine content, based on the feeding composition

4.4 Swelling Characteristic of the DAM-TAP gels

Not having hydrolysable groups, investigation of the swelling behaviors of the gels constituted with fully ionizable quaternary ammonium groups seemed to be very exciting because combination of nonhydrolysability and full ionizability was considered to be extremely beneficial for examination of the swelling characteristics in drastic conditions. According to our present knowledge, these gels are expected to show high swelling, as high as those for superabsorbents and rapid water sorptions. Indeed swelling of the gels is very interesting. The dried gel samples when soaked in water disintegrate with an audible cracking sounds of particles. The sounds continue for about 50 min and the gel samples turn into suspended small transparent particles. Obviously, this behavior can be ascribed to the high osmotic pressure due to strong ionic groups inside the gels. According to the network theory outlined by (Flory, P. J.1953) and by other authors (Hooper.H.H.1990) polymer–solvent interaction, polymer elasticity, and ionic effects govern swelling of the gels, polymer–solvent interaction can be neglected when ionic charge density is high enough. As a result, in these gels, there is a competition of high osmotic pressure

with the polymer elasticity. Since, in our case, the ammonium groups in the gels are close to each other, the ionic effect is far more superior to the elasticity and the polymer elasticity will not be able to hold the polymer in swollen state. As a result, excess osmotic pressure yields disintegration of the gel particles. In other words, in order to obtain gels of quaternary ammonium polymers with high swelling ability elastic segments must be incorporated by copolymerization or by other means. Of course, crosslinking density and salt effect are common effects on swelling. In [Figure B.1] swelling rates of DAM/TAP copolymers are in accordance with their crosslinking densities. But homopolymer of the crosslinker (TAP) itself differs from the others in that its swelling rate is higher than those of DAM-TAP (20%) copolymer in the first 20 min from the beginning. The difference can be ascribed to the charge densities. In the DAM-TAP copolymers the density of quaternary amine functions is in 4.1–4.28 mmol g^{-1} range, whereas it is 4.9 mmol g^{-1} for the homopolymer. So about 0.6 mmol of charge difference per gram must be responsible for the high swelling rate of the latter. Moreover, Peppas kinetic swelling formula $W/W` = kt^n$ (where $W`$ is weight of the gel at the equilibrium and W is the weight at time t. k and n are constants) gives 0.87–1.04 values for the n exponent, which is characteristic for ionic hydrogels. 26 This formula is valid in the swelling ratio less than 60%. Using this criteria the exponents, n, are obtained from the slope of the logarithmic plots [log (W/W_0) versus log t] as usual. [Figure B.2] shows salt effect on the swelling behaviors. As might be expected, the swelling rates and equilibrium swelling degrees become lower than in pure water. No disintegration is observed in the salt solutions. Also, HBr solution has the same effect with those of the KBr solutions (cf.bottom curve in Fig. B.2). In other words, acid solutions do not impose additional effect other than the salt effect, which is common for polyelectrolytes. Although, no remarkable effect is observed in dilute alkaline solutions at room temperature, the hydrogels become light yellow in color when boiled in 1*M* NaOH solution for 30 min. Most probably the colorination is because of the overall HBr elimination so called Hofmann's exhaustive methylation(Hoffman,A.W.Ber 1881) yielding vinyl residues.

4.5 Extraction of Anionic Dyes

Dye extraction experiments were carried out simply by contacting wetted gel

samples with aqueous dye solutions at room temperature. Capacities were assigned by colorimetrical analysis of residual dye contents.

4.5.1. Extraction of Anionic Dyes by DAM Gels

The hydrogel swelled in water shows reasonably high dye sorptions as high as 0.77 g per gram. More important is that, this material is able to remove the anionic dyes completely even from highly diluted aqueous dye solutions. No any trace absorbance was detected in the visible range, after processing. In other words, by this way, it is possible to obtain optically clear water by contacting with the hydrogel for 10-15 min.

Table 4.2. Sorption capacities of the DAM hydrogel with 10% TAP for some dyes

Dye	Initial conc. ($g.L^{-1}$)	Capacity (mg dye / g gel)	λ_{max} (nm)
Chalgone	0.20	84.0	545
Everzol Black	10.00	943	597
Everzol Blue RS/P	10.00	770	591
Everzol Red 3BS	10.00	950	539

It is important to note that the hydrogel can be used in a wide temperature range. For instance the capacity for Everzol Red 3BS does not change practically in pH range of 2.0-8.5.

4.6 Simple Analysis of the Result

Average mass of 0.9 mol DAM (Mw: 248) and 0.1 mol TAP (Mw: 408)

$$0.9 \times 248 + 0.1 \times 408 = 264 \text{ Da (g / mol)}$$

Quaternary group content :

$$0.9 + 2 \times 0.1 = 1.1 \text{ mol}$$

Quaternary group density:

$$1.1 / 264 = 4.16\ 10^{-3} \text{ mol / g} = 4.16 \text{ m.mol / g}$$

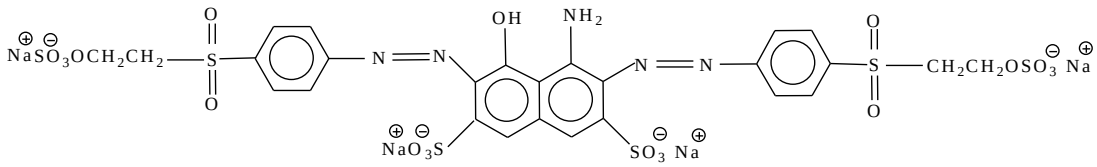
Since mol. Weight of Everzol black GSB is 991 Da as shown in Scheme 4.4, 963 mg of the sorbed dye

$$963 / 991 = 0.972 \text{ m.mol}$$

In the anionic dye every sulphon group attach with 4 molecules quaternary group so

$$4 \times 0.972 / 4.16 = 0.936$$

In other words, 1- 0.936 = 0.064 = 0.64 % of ammonium groups remain untouched during the dye sorption process or ~100 % of quaternary amonium groups react with dye .



Scheme 4.4 Structural formula of Everzol Black GSB

4.7 Effect of dye concentration on the capacity

Langmuir isoterm is applied for physical dye adsorption uptake .In this theory isoterm is proportional with dye concentation but in our experimant dye sorptions are practically independent of the initial dye concentrations shown in (Table 4.3). We observe the removal capacity of the gel not change with diffrent dye concentration, this shows us interaction between the dye and hydrogel is a chemical interaction

Table 4.3. Effect of dye concentration on the uptake capacity of gel

Dye concentration (g / L)	Everzol Black GSP	Everzol Red 3BS	Everzol Blue RS/P
10.00	0.963	0.950	0.870
5.00	0.921	1.030	0.813

3.33	0.979	1.060	0.848
2.50	0.928	0.953	0.824

4.8 Kinetics of the dye sorption

In order to estimate efficiency of the hydrogels for trace dye, batch kinetic experiments were performed using high diluted dye solutions (0.01 g L^{-1}). For this purpose the polymeric resins (0.1 g.) were wetted with distilled water (1.5 ml) and added to a solution of dye (100 ml of 0.1 g. dye in 90ml water). The mixtures were stirred magnetic stirring bar and aliquots of the solution (10 ml) were taken at appropriate time intervals for analysis of the residual dye contents by the method as described above. The results found in [Fig B.3]

4.9 Effect of pH

Dye sorption effect of different pH is estimated in our study. Study is made at the four different pH that 2.04, 4.05, 5.89, 8.74 at the same dye consantration(0.05 g/L) The results found in [Fig B.4]

4.10 Regeneration of the hydrogels

Most of dye sorbents are not regenerable. In this study we have attempted to regenerate the gels loaded. It was observed that, saturated NaCl solution, sulfuric acid have good effect in back- absorbtion of the gel-bound dye. Our preliminary experiments showed that, aniline is not effective in splitting of the sorbed dyes.

The dye loaded samples (0.2g.) were interacted with 10 ml of saturated sodium chloride (6 M) and stirred at 80^0C for 1h. after cooling, the mixtures were filtered, and 2 ml of the filtrate was taken out for colorimetric analysis of the dye. Results are shown in (Table 4.4).

Table 4.4 . Regeneration with different solution

Desorbing agent	**Temperature (^{o}C)**	**Time (h)**	**Recovered dye (mg/g)**	**Recovered dye (mg per g dye free gel)**	**Percentage Dye recovery**

1 M NaCl	50	3	248.8	488.4	50.7%
3 M NaCl	50	3	293.3	575.2	59.7%
5 M NaCl	50	3	419.0	822.5	85.4%
6 M NaCl (Saturated)	50	3	423	830.3	86.2%
4 M H_2SO_4	RT	24	79.6	156.2	16.2%
Aniline	80	24	Trace	Very low solubity in Aniline	

5.CONCLUSION

New cationic hydrogel obtained by copolymerization of DAM with TAP is a very efficient dye sorbent. Main pecularities of this material can be summarized as follows:

- These material shows unusually high dye uptake capacities as high as 1 g dye per gram of its dry weight
- It is efficient even for trace quantities of dye.
- The dye removal by this sorbent is so efficient that ; optically clear solutions can be attained within 10 minutes of the contact.
- Optimal pH range of the dye sorption is in pH: 6-8 range
- The desorption of the loaded dye can be achieved by saturated NaCl solution. Two or three times of treatment yield dye-free polymer.
- Regenerated hydrogels are reusable for further dye-uptakes. Although dye-sorption abilities of the regenerated samples have not been tested, it is likely that , these can be recycled used in further treatments.
- Considering with those pecularities, the new dye-sorbent is superior to common sorbents reported so far. Moreover regenerability of this material makes it very attractive in large scale waste water treatments.

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APPENDIX A

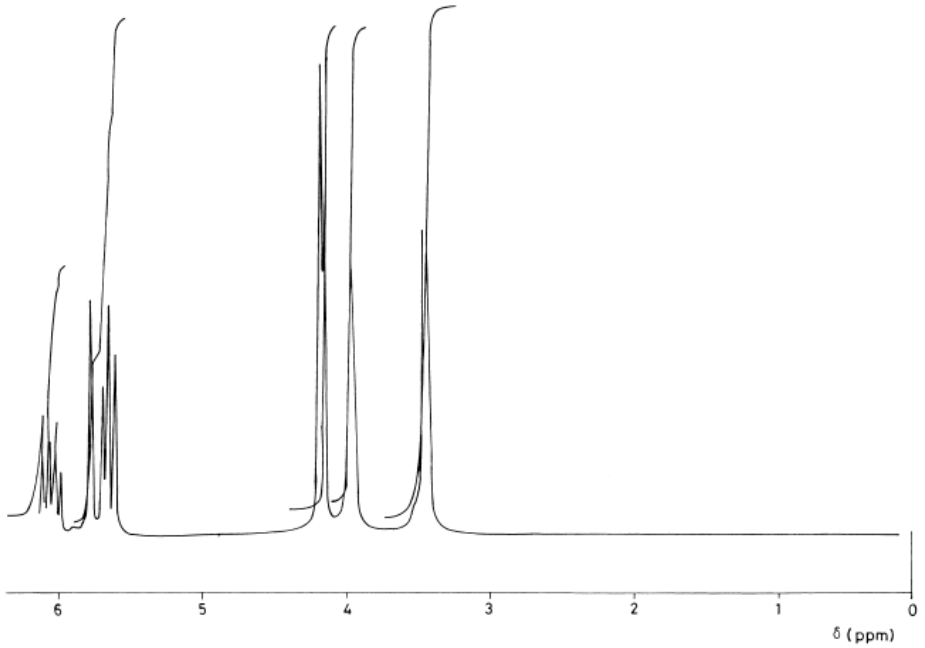


Fig A.1. ^{1}H-NMR Spectrum of N,N-Diallyl morpholinium bromide (DAM) in DMSO

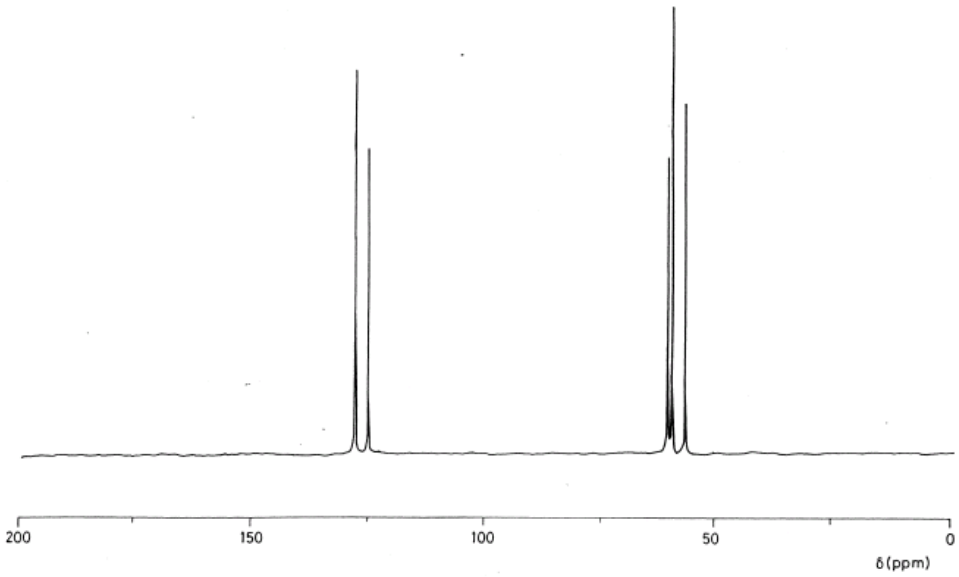


Fig A.2. ^{13}C-NMR Spectrum of N,N-Diallyl morpholinium bromide (DAM) in DMSO

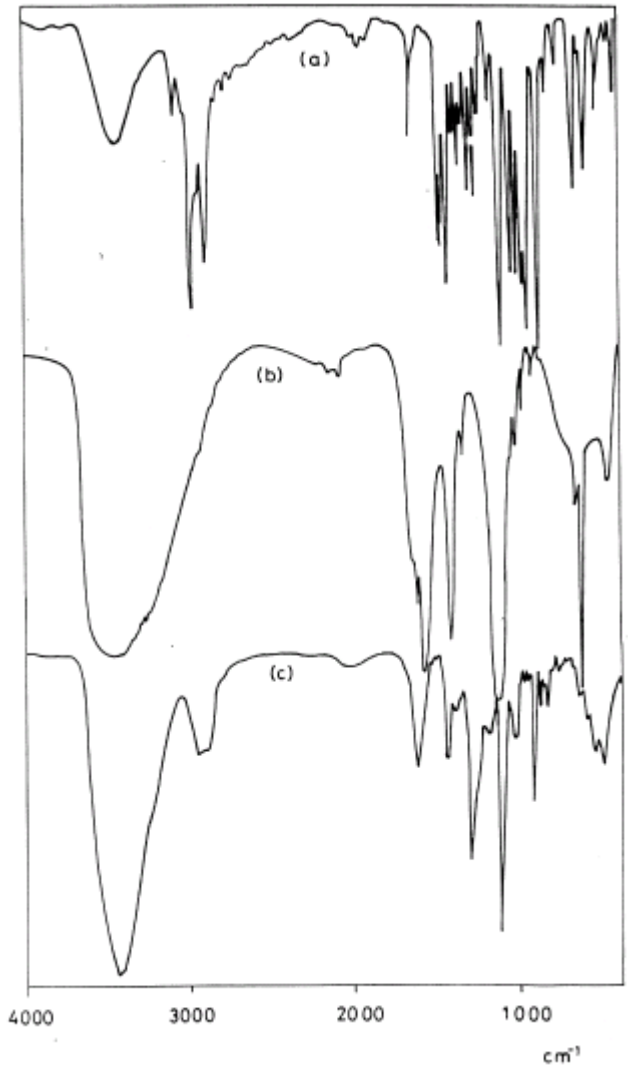


Fig A.3 FT-IR Spectrum of N,N-diallyly morpholinium bromide (DAM) (a), Homopolymer of DAM (b). The copolymer of DAM with sulfur dioxide (c)

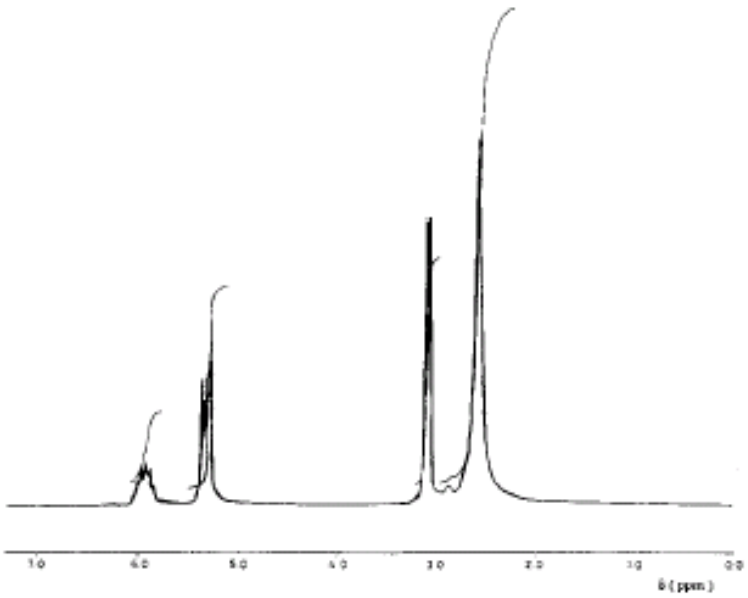


Fig A. 4. ^{1}H-NMR Spectrum of N,N-Diallyl piperazine bromide (DAP)

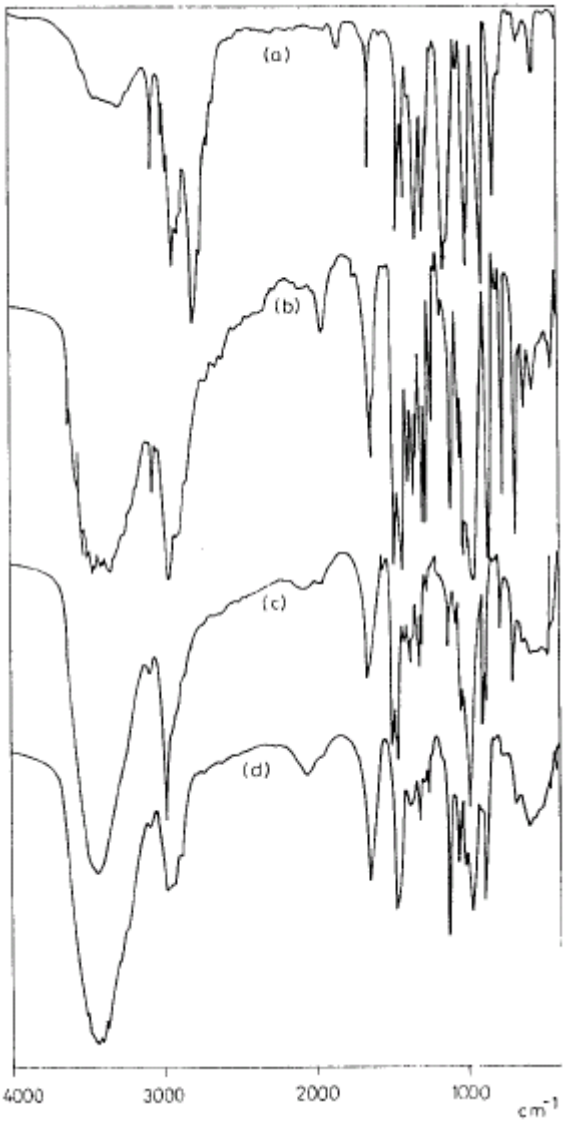


Fig A. 5. FTIR spectra of (a) N,N'-diallyl piperazine (DAP); (b) N,N,N',N'-tetra allyl piperazinium dibromide (TAP); (c)the homopolymer of N,N,N',N'-tetra allyl

piperazinium dibromide (TAP); (d) copolymer of TAP with N,N-diallyl morpholinium bromide (DAM).

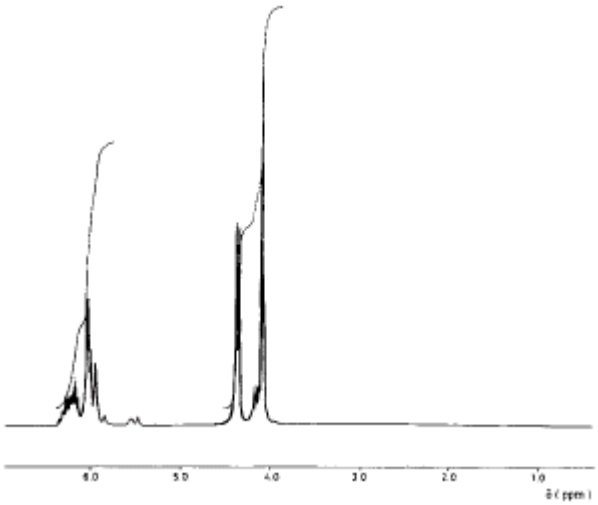
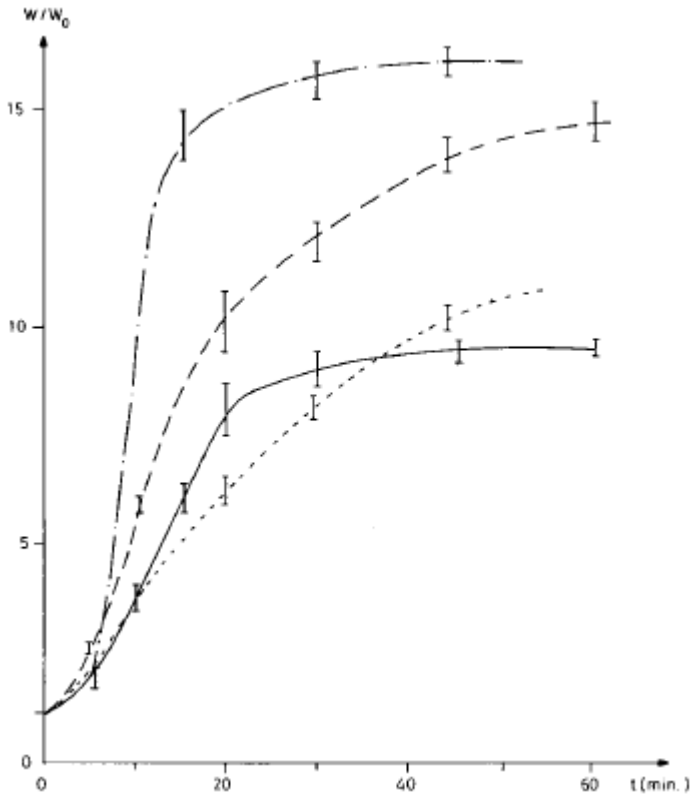


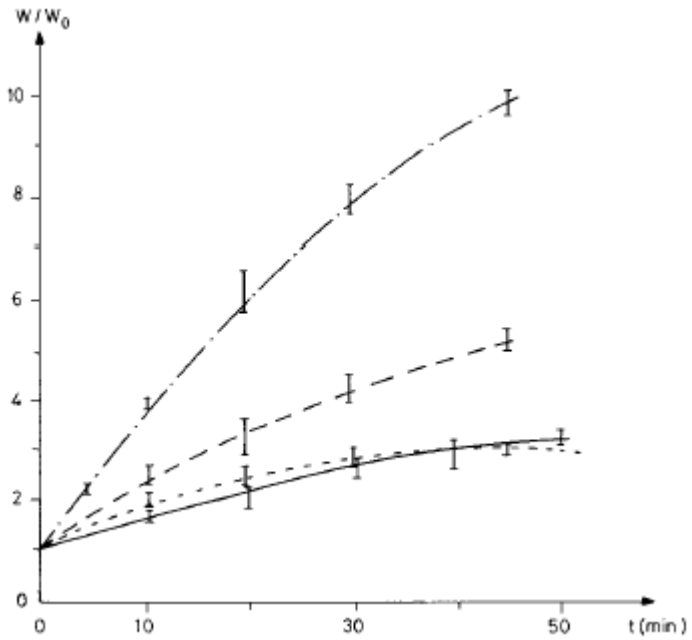
Fig A.6. ^{1}H-NMR spectra of N,N,N',N'-tetra allyl piperazinium dibromide (TAP)

APPENDIX B



5% crooslinker(__.__.__)10% crooslinker(- - -)
20% crooslinker(.....) 100% crooslinker(_____)

Fig B.1 Swelling kinetics of hydrogel



H_2O (__ . __ .__) , KBr (0.1 M) (- - -)
KBr(1.0 M) (. . .) HBr (1.0 M) solutions (____)

Fig B.2. Swelling kinetics of the hydrogel in different iyonik solution (10% croolinker)

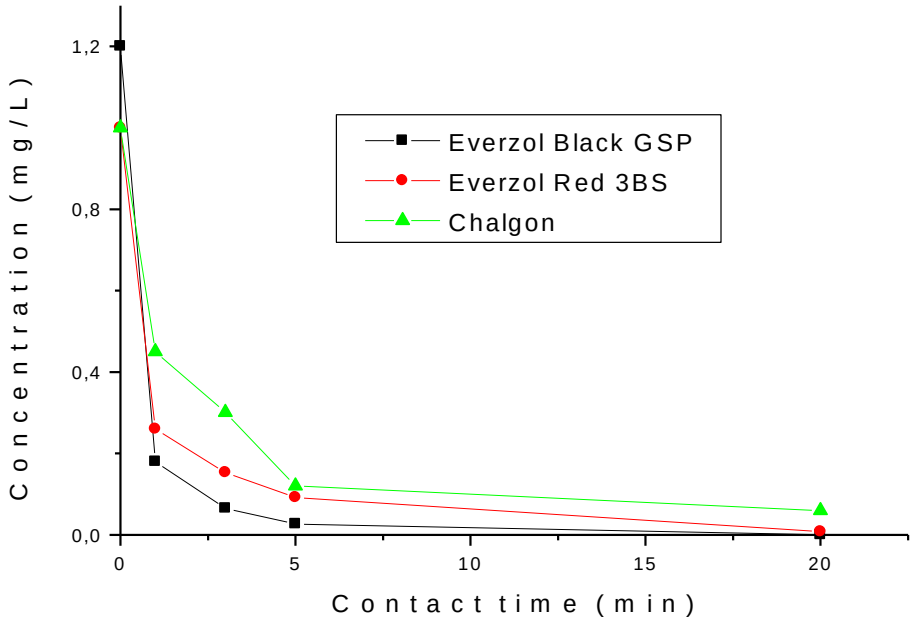


Fig B.3. Kinetic results of the hydrogel

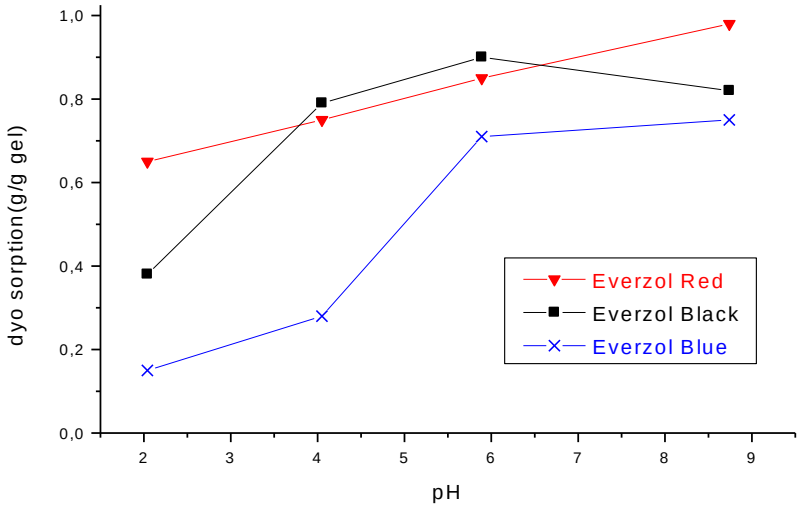


Fig B.4. Effects of different pH

AUTOBIOGRAPHY

He was born in 1977 in İstanbul. He graduated Yedikule High School and attended to the İstanbul Technical University Faculty of Science and Lecture Department of Chemistry . In 2002 , he began as a master student in İstanbul Technical University, Polymer Science and Technology. He still work in a rubbery sole manufacturer as a researcher.